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(54) Name of the invention: Flexible Polyolefin Type Resin Composition and Film  
Obtained by Using That

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*[ Note : Names, addresses, Company names and brand names are translated in the most common manner. Japanese Language does not have singular or plural words unless otherwise specified with numeral prefix or general form of plurality suffix. Translator's note.]*

**(54) [Name of the invention]**

**Flexible Polyolefin Type Resin Composition and a Film Using That**

**(57) [Summary]**

**[Goal]**

The goal of the present invention is to suggest a polyolefin type resin composition material that can form a film with excellent tensile strength, deformation recovery properties and stress relaxation properties, and to suggest a film made by using that.

**[Structure]**

A polyolefin type resin composition material is suggested that contains a polyolefin resin A in an amount in the range of 50 ~ 95 weight %, a polyolefin resin B or polyethylene type resin C, in an amount in the range of 50 ~ 5 weight %, and it suggests a film obtained from that composition. This polyolefin type resin A is a copolymer material that is formed from the following here below component (i) and (ii); (i) propylene, and/or a combination of propylene and alpha - olefin; (ii) ethylene, and/or a combination of ethylene and alpha-olefin. The above described polyolefin type resin B is a polyolefin resin that has a random branched molecular structure, and the above described polyethylene type resin C is obtained by polymerization using as a catalyst a metallocene compound containing tetravalent transition metal.

**[Scope of the claims of the present invention]**

**[Claim 1]**

It is a polyolefin type resin composition material that is a polyolefin type resin composition that contains a polyolefin resin A in an amount in the range of 50 ~ 95 weight % and polyolefin resin B, and where this polyolefin type resin A is a copolymer material that is formed from the following here below component (i) and (ii):

(i) propylene, and/or a combination of propylene and alpha - olefin;

(ii) ethylene, and/or a combination of ethylene and alpha-olefin;

and where the above described polyolefin type resin B is a polyolefin resin that has a random branched molecular structure.

[Claim 2]

Polyolefin type resin composition material that is a polyolefin type resin composition that contains a polyolefin resin A in an amount in the range of 50 ~ 95 weight %, and a polyethylene type resin C, in an amount in the range of 50 ~ 5 weight %,

and where this polyolefin type resin A is a copolymer material that is formed from the following here below component (i) and (ii);

(i) propylene, and/or a combination of propylene and alpha - olefin;

(ii) ethylene, and/or a combination of ethylene and alpha-olefin; and where the above described polyethylene type resin C is obtained by polymerization reaction using as a catalyst a metallocene compound containing tetravalent transition metal.

[Claim 3]

Polyolefin type resin composition material according to the above described Claim 1 or Claim 2 of the present invention, where the above described polyolefin type resin A is manufactured by a multi-step polymerization method where the component (i) is initially polymerized.

[Claim 4]

Polyolefin type resin composition material according to the above described Claim 1 or Claim 3 of the present invention, where an experimental piece of the above described polyolefin type resin B is introduced into a melting - extension study at a extension scanning rate in the range of 0.01 ~ 1.0 s<sup>-1</sup>, and at the time when the amounts of extension occurring at two points, a (0.1 ≤ a ≤ 1.0) and b, is 1 : 10, the melting extensional viscosities  $\eta_a$  and  $\eta_b$  satisfy the following here below relation

[1]

$$3.0 < = \frac{11.6}{2.9} < = 100 \dots\dots\dots \text{equation (I)}$$

and then, the above described polyolefin type resin B does not contain a gel type component.

[Claim 5]

Polyolefin type resin composition material according to the above described Claim 2 or Claim 3 of the present invention, where the above described polyethylene type resin C has a density that is in the range of 0.860 ~ 0.950 g/cm<sup>3</sup>, and where according to the cross separation method, the range from the temperature at the time when 10 weight % are eluted to the temperature when 100 weight % are eluted and it is completed, is within 30°C, and its molecular weight is in the range of 1.5 ~ 3.5.

[Claim 6]

Film material that is formed from the polyolefin type resin composition materials reported according to any of the above described Claims 1 through 5.

[Detailed description of the invention]

[0001]

[Technological sphere of application]

The present invention is an invention about a polyolefin type resin composition material that forms a film with excellent tensile strength, deformation recovery properties, and stress relaxation properties, and excellent elastic (flexibility) properties, elongation properties, and thermal resistance properties. And in more details, the present invention is an invention about a resin composition materials that contains a flexible polyolefin type resin, a polyolefin type resin with a random branched type molecular structure, or a polyethylene type resin that has been polymerized under the presence of a metallocene compound containing a tetravalent transition metal, used as a catalyst material; and it is about the film materials obtained by using these resin compositions.

[0002]

[Previous technology]

As resin materials that are appropriate for different types of films that are flexible and that have elongation and contraction properties, there are the plasticised vinyl chloride materials (here below called plasticised PVC). If a film is produced by using the above described plasticised PVC, this film usually, contains a large amount of plasticising agent and because of that the plasticising agent is transferred to the front surface, and it has a deterioration effect on the properties, etc. In recent years, the problems with the environment have also become important, and the use of plasticised PVC, which is halogen containing polymer material, has been called in different areas, and the research regarding replacement materials has exploded.

[0003]

Because of that, as a replacement material for the plasticised PVC material, the invention of polyolefin type resins has been heavily conducted. For example, films that have made use of polyethylene (PE), ethylene-vinyl acetate copolymer material, polybutadiene etc., polyolefin type resins, have been manufactured. However, in the case of the films that have advantageously used these type of materials, for example, the elastic properties, the deformation recovery properties, and the required in the film stress relaxation properties are insufficient.

[0004]

Consequently, in the case of packaging films there is a quick separation, and there is a generation of wrinkles in the film, or on the contrary, the stress is too high, and there are many cases when these films cannot be used appropriately in practical applications.

[0005]

As a method in order to impart flexibility properties onto polyolefin type resins, especially, polypropylene type resins, the method is widely known where this is improved by the crosslinking of the elastomer and polypropylene mixed material. For example, in the Japanese Patent Application Laid Open Number Hei-Sei 1-247441, as a bumpers, etc., automobile part products, an elastomeric resin material is disclosed that is obtained as an elastomer obtained from ethylene - alpha - olefin and polypropylene, are crosslinked (cured) under the presence of a crosslinking agent.

[0006]

Regarding the above described elastomeric crosslinked resin material, it is a material that has excellent tensile strength and elastic properties, however, because this is an afterblend, the elastomer component is not sufficiently

dispersed into the polypropylene, and in order to maintain good dispersibility properties, the molecular weights of the correspondingly used elastomer material and polypropylene material are confined to a particular range, and the flexibility properties and the elongation of the obtained crosslinked resin material, is insufficient. Then, in the case of the above described crosslinked resin material, it is not satisfactory for applications other than the injection molding.

[0007]

As polyolefin type resin materials that can form film materials by using other methods besides the injection molding method, according to the reported in the Japanese Patent Report Laid-Open, Number Showa 59-50172, a resin has been disclosed, that is obtained by the crosslinking treatment of ethylene copolymer material or crystalline polypropylene and a specific ethylene - acrylate type polymer copolymer material. Regarding this resin material, it is a material that has as an essential component any one of the following materials: ethylene - vinyl acetate copolymer, ethylene - acrylic acid ester copolymer, ethylene - methacrylic acid ester, ethylene - methacrylic acid copolymer, or ethylene - acrylic acid copolymer material. The above described copolymer materials contain copolymerization components like acrylic acid or vinyl acetic acid, and because of that, the resin material has insufficient thermal resistance properties and flexibility properties, and a good film is not obtained.

[0008]

For the improvement of the flexibility properties of polyolefin type resins, the method is usually used where the proportion of the elastomer material in the copolymer, is increased. However, in the case when the above described crosslinking treatment is conducted, it is accompanied by a mechanical mixing operation by using an extruder, etc., and because of that, the costs are increased. Then, in the case when the elastomer component has a high molecular weight, it is agglomerated and it is not sufficiently dispersed, and because of that, the molecular weight of the used elastomer material, is limited. Because of that, the resin material that has been subjected to the above described mechanical mixing operation, has insufficient flexibility properties, deformation recovery properties, etc., different types of properties, and the situation is such that a good film material cannot be obtained.

[0009]

There are also the elastomer where in a linear chain type polyethylene, different types of alpha-olefins are copolymerized (Japanese Patent Application Laid-Open Number Showa 61-44635) or the styrene containing elastomer conjugated diene type elastomer material (Japanese Patent

Application Laid-Open Number Showa 62-51440). However, in the case when either of these is used individually, thermal resistance properties and elongation and contraction properties are not obtained, and it is necessary that another resin is laminated as a laminated layer, and it is not appropriate for film applications.

[0010]

**[Problems solved by the present invention]**

The goal of the present invention is to suggest a polyolefin type resin composition material that can form a film with excellent tensile strength, deformation recovery properties and stress relaxation properties, and to suggest a film made by using that.

[0011]

**[Measures in order to solve the problems]**

According to the first invention, of the present invention, it is a polyolefin type resin composition material that is a polyolefin type resin composition that contains a polyolefin resin A in an amount in the range of 50 ~ 95 weight %, a polyolefin resin B or polyethylene type resin C, in an amount in the range of 50 ~ 5 weight %, and where this polyolefin type resin A is a copolymer material that is formed from the following here below component (i) and (ii):

(i) propylene, and/or a combination of propylene and alpha - olefin;

(ii) ethylene, and/or a combination of ethylene and alpha-olefin;

and where the above described polyolefin type resin B is a polyolefin resin that has a random branched molecular structure.

[0012]

According to the second invention, of the present invention, it is a polyolefin type resin composition material, that contains a polyolefin resin A in an amount in the range of 50 ~ 95 weight %, and a polyethylene type resin C, in an amount in the range of 50 ~ 5 weight %, and where the above described polyethylene type resin C is obtained by polymerization using as a catalyst a metallocene compound containing tetravalent transition metal.

[0013]

In the case of the preferred practical implementation conditions, the above described polyolefin type resin A is manufactured by a multi-step polymerization method where the component (i) is initially polymerized.

[0014]

In the case of the preferred practical implementation conditions, an experimental piece of the above described polyolefin type resin B is introduced into a melting - extension study at a extension scanning rate in the range of  $0.01 \sim 1.0 \text{ s}^{-1}$ , and at the time when the amounts of extension occurring at two points, a ( $0.1 \leq a \leq 1.0$ ) and b, is 1 : 10, the melting extensional viscosities  $\eta_a$  and  $\eta_b$  satisfy the following here below relation

[1]

$$3.0 \leq \frac{\eta_b}{\eta_a} \leq 100 \dots\dots\dots \text{equation (I)}$$

and then, the above described polyolefin type resin B does not contain a gel type component.

[0017]

In the case of the preferred practical implementation conditions, the above described polyethylene type resin C has a density that is in the range of  $0.860 \sim 0.950 \text{ g/cm}^3$ , and preferably in the range of  $0.870 \sim 0.945 \text{ g/cm}^3$ , and also according to the cross separation measurement method, the range from the temperature at the time when 10 weight % are eluted to the temperature when 100 weight % are melted and eluted and it is completed, is within  $30^\circ\text{C}$ , and preferably, it is within the range of  $28^\circ\text{C}$ , and then, also its molecular weight is in the range of  $1.5 \sim 3.5$ , and preferably, it is in the range of  $1.7 \sim 3.0$ .

[0018]

Then, the film material according to the present invention is a material that is formed from the above described polyolefin type resin composition materials.

[0019]

Here below, the present invention will be described in more details.

[0020]

Regarding the polyolefin type resin A, that is used according to the present invention, it is a copolymer material that is obtained from (i) propylene

and/or a combination of propylene and alpha-olefin, and together with that, (ii) ethylene and/or a combination of ethylene and alpha-olefin. Consequently, the polyolefin type resin A is a copolymer material that contains polyolefin type resin A, propylene, ethylene and depending on the requirements, alpha-olefin components. This resin material A is a material that contains in its molecule, polypropylene blocks generated as only propylene component is bonded, polyethylene blocks, alpha-olefin blocks, ethylene - alpha-olefin blocks, that are generated as ethylene and alpha-olefin are bonded, etc. As the alpha-olefin component, it is possible to use 1-butene, 1-pentene, 1-hexene, 4-methyl - 1- pentene, etc.

[0021]

As the block component that is present in the resin A according to the present invention, as the (i), propylene and/or a combination of propylene and alpha-olefin, for example, there are the following: propylene homopolymer block, or propylene / ethylene, propylene/ butene - 1, and propylene/ 4-methyl - 1-pentene, etc., 2 basic copolymer blocks, or propylene/ethylene/butene - 1, and propylene/butene - 1/4-methyl -1- pentene, etc., 3 basic polymer blocks, etc.

[0022]

As the block components that are present in the above described resin material A, as the (ii), ethylene and/or ethylene and alpha-olefin combination, there are ethylene homopolymer blocks, or ethylene and alpha-olefin copolymer blocks, for example, ethylene/butene-1, ethylene/hexene-1, 4-methyl-1-pentene block, etc.

[0023]

The polyolefin type resin A, that is used according to the present invention can be manufactured, for example, according to the described here below multi-step polymerization method. First, as the first step, under the presence of titanium compound catalyst and aluminium compound catalyst, by using the (i) component propylene monomer and depending on the requirements, by using the alpha-olefin monomers, a polymerization is conducted. From these, propylene homopolymer materials, propylene - alpha-olefin copolymer materials, etc., are formed. After that, as the second step, at a state where a titanium compound catalyst is contained, for example, in a reaction solution that contains the above described homopolymer material or copolymer material, the above described component (ii) is added and a copolymerization is conducted, and by that the polyolefin type resin A is obtained. At this time, it is also a good option if the (ii) component is added, even though it has been added at the first step. The polyolefin type resin A that has been obtained according to the above described multi-step reaction is obtained as a propylene - ethylene copolymer, propylene - alpha - olefin copolymer, or propylene -

ethylene - alpha-olefin copolymer material. As it is described here below, in correspondence to the goals, the multi-step copolymerization reaction is conducted. The characteristics of this manufacturing method are that the polymerization is not completed in a one step process, and that a two or more multi-step polymerization process is conducted. By that, it is possible to continually manufacture a number of different polymer materials, and it becomes completely different from the usual polymer blend obtained by the mechanical mixing process, and a copolymer material is formed that is like an intermolecular blend.

[0024]

In the case of the usual polymer blend, in order to increase the flexibility properties and the elongation and contraction properties, there is one method according to which a high molecular weight elastomer component is mixed. However, in the case of a polymer blend obtained according to the usual mechanical mixing, the high molecular weight elastomer has high melt viscosity and because of that, a composition material that has a structure where the elastomer component is finely dispersed, is not obtained. Because of that, contrary to that, in the case of the polyolefin type resin A that is used according to the present invention, the above described component (i) is an elastomer component, namely, it has a structure where a phase of a soft (flexible) part, is formed. And this component (ii), has a high molecular weight and because of that it has high melt viscosity, however, by using the above described multi-step polymerization method, it is possible that a molecular structure is obtained where the above described component (i) and component (ii), namely, the hard part phase and the soft part phase, are finely dispersed.

[0025]

In the case of propylene and olefin type block copolymer material that has been obtained according to the polymerization methods of the previous technology, it is a material where the ethylene, alpha-olefin, etc., that are copolymerized as a flexible properties imparting component and where the main component is polypropylene. And in that type of manufacturing process, the amount contained of the polypropylene, which represents the main component, is limited to a content of approximately 50 weight %, and usually its content is up to 30 weight %. Because of that, in the case of the above described block copolymer material, the practical realization of flexible properties as those in the case of the plasticised PVC, is extremely difficult. Contrary to that, according to the above described multi-step polymerization process, it becomes possible that the above described copolymerized component is contained up to an amount in the range of approximately 80 ~ 95 weight %, and by that a polyolefin type resin material is obtained that has the same properties as a plasticised PVC.

[0026]

As such manufacturing method, for example, there is the manufacturing method that has been reported according to the Japanese Patent Application laid-Open Number Hei-Sei 4-224809. According to this method, as the titanium type compound, for example, it is possible to use granulated type, solid phase titanium catalyst that has an average particle diameter of 15 microns, and that is obtained as a powder material that is obtained by pulverizing (grinding) together titanium trichloride and magnesium chloride, and then this is treated by using n-butyl ortho titanate, 2-ethyl-1-hexanol, methyl ester of the p-toluenic acid, silicon tetrachloride, isobutyl phthalate. etc. According to this method, then, in the polymerization vessel, as an electron acceptor material, a silicon type compound, especially, diphenyl dimethoxy silane, is added, and then, an iodized ethyl is added. Then, in the description of the Japanese Patent Application Laid-Open Number Hei-Sei 4-283252, the titanium compound, the use of magnesium chloride and alcohol adduct compound treated by using titanium tetrachloride and an electron acceptor material, has been reported. In the description reported in the Japanese Patent Application Laid-Open Number Hei-Sei 4-266954, the method using the described here below catalyst, has been disclosed: a catalyst where on an active form bi-halogenated magnesium, at least one halogen - titanium bond containing titanium compound and an electron acceptor material are supported. Besides these methods, also, for example, such manufacturing methods have been described in the reported according to the Japanese Patent Application Laid-Open Number Hei-Sei 4-96912, Japanese Patent Application Laid-Open Number Hei-Sei 4-96907, Japanese Patent Application Laid-Open Number Hei-Sei 3-174410, Japanese Patent Application Laid-Open Number Hei-Sei 2-170803, Japanese Patent Application Laid-Open Number Hei-Sei 2-170802, Japanese Patent Application Laid-Open Number Hei-Sei 3-205439, and Japanese Patent Application Laid-Open Number Showa 61-42553, etc. At the time of the manufacturing of the polyolefin type resin A that is contained in the composition material according to the present invention, as in the above described, any of the well known methods can be used. As commercially available products of resin materials that have been obtained according to such manufacturing methods, the "PER", manufactured by Company. and the "Cataloy", manufactured by Himont Company, etc., are available. And any of these materials can be used according to the present invention.

[0027]

Then, regarding the above described polyolefin type resin A, usually, according to the cross separation method, the melting eluted component at a temperature of 90°C or above is in the range of 5 ~ 50 weight %. In the case when the above described melted eluted component is less than 5 weight %,

the molded material that is obtained by using the obtained composition material, for example, film, has insufficient tensile strength properties. And in the case when the above described melted eluted component exceeds 50 weight %, whitening and necking occur and the extensional properties are decreased.

[0028]

Regarding the polyolefin type resin B that is used according to the present invention, it is a material that has a random branched molecular structure. Regarding this molecular structure, it is not a structure that is particularly limited, and it is a material that can have any type of branched part. At the time when an experimental piece of the above described polyolefin type resin B is introduced into a melting - extension study, at an extension scanning rate in the range of  $0.01 \sim 1.0 \text{ s}^{-1}$ , when the amounts of extension occurring at two points,  $a$  ( $0.1 \leq a \leq 1.0$ ) and  $b$ , is  $1:10$ , the melting extensional viscosities  $\eta_a$  and  $\eta_b$  satisfy the following here below relation.

[0029]

[3]

$$3.0 < \frac{\eta_b}{\eta_a} < 100 \dots\dots\dots \text{equation (I)}$$

[0030]

Regarding this melt extension viscosity, for example, it can be obtained by conducting a melting extension experiment by using Melten Rheometer (manufactured by Toyo Seiki Company). In more details, the experimental method is presented in the practical implementation examples. However, the schematics are according to the following here below. At a temperature that exceeds the melting point of the resin, a cylindrically shaped resin experimental material, is extended uniaxially, and the extension strain and extensional stress at the time of the melting, are measured. Regarding the melt extensional stress and the melt viscosity, there is the following relationship: (melt viscosity) = (melt extensional stress) / (deformation rate). And because of that, according to the present invention, the above described melt extension stress is defined as the melt extension viscosity. In the case of a resin material that has a random branched molecular structure such as that of the polyolefin type resin B according to the present invention, this melt extensional viscosity is increased at the time of a large deformation. Consequently, as it is shown according to the equation (I), the value of  $b/a$ , becomes a large value that is in the range of  $3.0 \sim 100$ . Regarding such increased viscosity at the time of a large deformation, it is due to the binding

and combining of the molecules of the above described polyolefin type resin B to each other. Regarding the results from the binding and combining of the resin material B, the composition material that includes the resin material B, demonstrates excellent elastic recovery properties at the time of inflation molding. Consequently, the resin composition material according to the present invention shows stable inflation molding properties. And then, in the case when packaging generating material is obtained, the packaging stability properties, are excellent.

[0031]

Regarding the above described polyolefin type resin B, preferably, it does not contain gels at all. The gel fraction is indicated by the gel fraction coefficient, as shown according to the described here below practical implementation example. Regarding the gel fraction, it is indicated by the insoluble part obtained in xylene under a high temperature. The polyolefin resin B according to the present invention has 0 % gel fraction obtained according to this test, and it does not contain a gel fraction at all. Because of the fact that it is a material that does not contain a gel fraction at all, the above described effect of the binding and combining of the polyolefin type resin B, is increased. Consequently, from the composition material according to the present invention, that contains the resin material B, it is easy to obtain commercial product film materials, by using the inflation molding method. Then, also, in the case when package generation materials are obtained, the package stability properties, are excellent.

[0032]

Regarding the above described polyolefin type resin B, polypropylene homopolymer material, or copolymer material containing propylene as the main component, and then also any type of mixtures thereof, can be used. This copolymer material, can be obtained by a copolymerization or a graft copolymerization. As this copolymer material, for example, polypropylene - alpha-olefin copolymer, containing 85 % or more of the polypropylene part, can be used. As the alpha-olefin that is used as the component in the above described copolymer material, ethylene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-butene, 1-hexene, etc., can be used. Regarding the random branched molecular structure possessing polyolefin type resin material, it can be appropriately manufactured according to the methods disclosed in the Japanese Patent Report Laid Open Number Showa 62-121704 or Japanese Patent Report Laid Open Number Hei-Sei 2-298536. According to these manufacturing methods, to the polypropylene an electron beam radiation or peroxide treatment is applied, and by that the random branched molecular structure is formed. According to these inventions, the the polyolefin type resin materials that have a random branched molecular structure, can be appropriately used as a coating material, oriented films, and blown films.

[0033]

Regarding the polyethylene resin C, that is used according to the present invention, it is a material that is polymerized by using as a catalyst a metallocene compound that contains a tetravalent transition metal.

[0034]

As the tetravalent transition metals, it is possible to use titanium, zirconium, nickel, palladium, hafnium, platinum, etc. And the compounds where to that tetravalent transition metal, one or more cyclopentadienyl rings and their derivatives are bonded as ligands, are usually called metallocene compounds.

[0035]

As the above described cyclopentadienyl ring derivative materials, cyclopentadienyl rings substituted by a hydrocarbon radical, a substituted hydrocarbon radical or a hydrocarbon - substituted metalloïd radical, cyclopentadienyl oligomer ring, indenyl ring, and indenyl ring substituted by a hydrocarbon radical, a substituted hydrocarbon radical or a hydrocarbon - substituted metalloïd radical, etc., can be used. As the above described ligands, it is possible to use chlorine, bromine, etc., monovalent anion ligands, or bivalent anion chelate ligands, hydrocarbon, alkoxide, aromatic or aliphatic amide, aromatic or aliphatic phosphide, etc. Regarding representative materials for the above described hydrocarbon radicals, there are the following: methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethyl hexyl, and phenyl.

[0036]

As the metallocene compounds that have above described coordinated ligands, cyclopentadienyl titanium tris (dimethylamide), methyl cyclopentadienyl titanium tris (dimethylamide), bis (cyclopentadienyl) titanium dichloride, dimethyl silyl tetramethyl cyclopentadienyl -tert-butylamide zirconium dichloride, dimethyl silyl tetramethyl cyclopentadienyl -p-n-butylphenylamide dizirconium dichloride, methyl phenylsilyl tetramethyl cyclopentadienyl -tert-butylamide hafnium dichloride, indenyl titanium tris (dimethylamide), indenyl titanium tris (dimethylamide), indenyl titanium tris (diethylamide), indenyl titanium tris (di-n-propylamide), indenyl titanium bis (di-n-propylamide), etc., can be pointed out as examples.

[0037]

Regarding the polymerization of the above described polyethylene type resin C, usually, as a co-catalyst to the above described metallocene compound, a catalyst was obtained as methylaluminoxane (MAO), boron element type compound etc., were added. The amount used of the co-catalyst compound, relative to the metallocene compound, was in the range of 10 ~ 1,000,000 mole times, and preferably, it was in the range of 50 ~ 5,000 mole times. There are no particular limitations regarding the polymerization method, and the solution polymerization method using an inert solvent type medium, or the agglomeration polymerization method, where practically there is no presence of inert solvent medium, gas phase polymerization method, etc., can be used. As the polymerization temperature, usually a temperature is used that is in the range of 100°C ~ 300°C, and as the polymerization pressure, usually a pressure is used that is in the range from a normal pressure ~ 100kg/cm<sup>2</sup>. Because this polymerization reaction has a homogeneous reaction activation point, a resin material is obtained that has the same molecular weight and the same degree of branching, and then, it is a resin material that has no variation in its crystallinity properties. Then, according to this reaction, at the time of the copolymerization the copolymerization components are introduced in a homogeneously dispersed state, and because of that, a molecule with effective branching is synthesized. Consequently, in the case of the obtained according to this reaction polyethylene type resin C, the molecular weight distribution is narrow and in each molecule, evenly, the copolymer component is introduced. And as a result from that a resultant confrontational bond (a molecule that bonds the crystalline part and the non-crystalline (amorphous) part) is synthesized, and because of that the surface impact properties are dramatically increased. Also, because the molecular weight distribution is narrow and a low molecular weight component is not contained, a low crystallinity polyethylene is obtained where there is no generation of adhesion etc. As such polyethylene type resin C, the CGCT, manufactured by Dow Chemical Company, the EXACT, manufactured by Exxon Chemical, etc., are available as commercial products. Contrary to that, in the case of the polymerization by using the usual Chigura - Nata catalyst material, when a copolymer material is obtained from ethylene and alpha-olefin, in that case, in the alpha-olefin that is in the copolymer material, there is a large amount of low molecular material fraction present, and there is almost no high molecular weight material, present. As a result from that, a high crystallinity component (hard phase part) and a low crystallinity component (soft phase part) are present mixed in the resin material. And because of that, the separation between the crystals becomes uneven, and the generation of the confrontational bond is hindered. Also, because the molecular weight distribution and the distribution of the copolymer components, are wide, in the case of the low crystallinity polyethylene material (polyethylene with a large amount of copolymerization component), because of the adverse effect of the low molecular weight component, there is a generation of a large number of problems like adhesion, odor, etc., and there are many problems in the practical applications.

[0038]

Regarding the above described polyethylene type resin C, it is a material that has a density that is in the range of  $0.860 \sim 0.950 \text{ g/cm}^3$ , and preferably, it is in the range of  $0.870 \sim 0.945 \text{ g/cm}^3$ . Then, regarding the measurement by the cross separation method, the range from the temperature at the time when 10 weight % are melted and eluted to the temperature when 100 weight % are melted and eluted, and it is completed, is within  $30^\circ\text{C}$ , and preferably, it is within the range of  $28^\circ\text{C}$ , and its molecular weight is in the range of  $1.5 \sim 3.5$ , preferably, it is in the range of  $1.7 \sim 3.0$ . In the case when the above described density is less than  $0.860 \text{ g/cm}^3$ , the crystallinity properties of the resin material are decreased, and the thermal resistance properties of the obtained resin composition material, are decreased. In the case when the above described density exceeds  $0.950 \text{ g/cm}^3$ , the crystallinity properties become high, and the dispersion state becomes poor, and the stress relaxation properties of the obtained resin material are decreased. If the above described temperature range exceeds  $30^\circ\text{C}$ , in the above described resin material, there are a high crystallinity part and a low crystallinity part present at the same time in the above described resin material C, and the stress relaxation properties of the resin composition material are decreased. If the above described molecular weight distribution is less than 1.5, the attainment of a dispersed state of the hard phase part and the soft phase part inside the obtained resin composition material, becomes poor, and the extensional properties are decreased. If the above described molecular weight distribution exceeds 3.5, the ratio of the molecules that have a molecular weight that is too low and the molecules that have a molecular weight that is too high, becomes high, and the stress relaxation properties, are decreased.

[0039]

According to the present invention, in correspondence with its goals, it is also a good option if in the above described polyethylene type resin C, other thermoplastic resin materials are added at a proportion that is in the range of  $0 \sim 20 \text{ weight } \%$ , for example, low density polyethylene, linear chain type low density polyethylene, medium density polyethylene, high density polyethylene, polypropylene, ethylene - propylene rubber, polyvinyl acetate, polybutene, etc.

[0040]

Regarding the above described cross separation method, it is a method that is appropriately used for the characterization of the above described resin materials A ~ C. This cross separation method, is a method that includes : (1) the Temperature Rising Elution Fractionation (TREF) method where the crystallinity distribution of the polyethylene type resin material C is

measured according to the above described method, and (2) the measurement of the molecular weight and the molecular weight distribution by a high temperature type GPC. Regarding this cross separation method, for example, it can be conducted by using the cross separation chromatography equipment (CFC - T150 A model: manufactured by Mitsubishi Petrol Company) that is equipped with the above described TREF equipment and a high temperature GPC (namely, SEC = size exclusion chromatograph).

[0041]

In the resin composition according to the present invention, in correspondence with its goals, it is also possible to incorporate anti-oxidation agents, stabilization agent, pigmenting agent, anti-clouding agent, anti-electrostatic agent, fireproof agent, etc. As the antioxidation agent and the stabilization agent, it is possible to use commercially available phenol type oxidation resistance agents, phosphorus type anti-oxidation agents, amine type anti-oxidation agents, sulfur type anti-oxidation agents, etc., compounds that are used in the preparation of high molecular weight compounds in order to prevent the deterioration from oxidation. And these materials can be used individually, or they can be used in a combination. Then, depending on the requirements, it is also possible to use carbon black, clay, talc, calcium carbonate, alumina, silica, kaolin, graphite, glass fiber etc., filler agents. Regarding the mixing of the above described materials, it can be practically realized by using an extruder, a Bumberry mixer equipment, roll, Brabender Plastograph, kneader, etc., well known mechanical melting and mixing operations.

[0042]

The film according to the present invention is obtained from the above described resin composition material by using an inflation molding (forming) method or a T die molding method. In the above described molding, it is possible to use a single or a number of extruders, a single extruder and a coextruder, extruder - lamination, etc., methods.

[0043]

Regarding the film that is obtained by such methods, it is a film that has excellent tensile strength properties, deformation recovery properties, and stress relaxation properties, and it has excellent flexibility properties, elongation properties, and thermal resistance properties.

[0044]

This polyolefin type film can be used individually or it can be used as it is laminated with another resin as long as that does not hinder the results according to the present invention.

[0045]

[Effect]

The polyolefin type resin A that is used according to the present invention, as it has been described earlier, is obtained by the copolymerization where to the polypropylene that forms the structure of the hard phase, ethylene and/or alpha-olefin is copolymerized that forms the structure of the soft phase, and preferably, it is obtained according to a multi-step polymerization. Consequently, the above described polyolefin type resin A is different from the polypropylene/ elastomer blend according to the previous technology, namely, the blend that is obtained by mechanical mixing, and the ethylene-alpha-olefin copolymer part that is the part that imparts the soft properties, is phase melted at a molecular level, and because of that, in the case of the above described polyolefin type resin A, homogeneous and extremely fine dispersed state is achieved.

[0046]

In the case of the random branched molecular structure possessing polyolefin type resin B that is used according to the present invention, a large part of its molecular chain exists as a non-crystalline (amorphous) part, namely, as a soft part. As a result from the tying and entangling of the above described soft branched molecular chains, the above described polyolefin type resin B has a significantly increased melt extension viscosity at the time of large deformation, compared to the obtained according to the previous technology usual, widely used polypropylene type resins.

[0047]

Usually, when the polyolefin type resin and the above described polyolefin type resin B, are mixed, the soft, branched molecular chain of the resin B is dissolved in the phase of the non-crystalline part in the above described polyolefin type resin material. And as a result from that, the effect of the entangling of the molecular chains inside the resin composition material, is increased, and an increase of the tensile strength and the deformation recovery properties, is anticipated.

[0048]

When a resin, like the above described polyolefin type resin A according to the present invention, that has a is homogeneous and very finely dispersed

state of the amorphous part, and the polyolefin type resin B, are mixed, the soft branched molecular chain of the resin B is phase dissolved in the amorphous part of the resin A, that is in a finely dispersed state at a molecular level, and at an extremely finely dispersed state an entangling of the molecular chains occurs, and the effect of the entanglement is significantly increased. And because of that, it is anticipated that the tensile strength and the deformation recovery properties are significantly increased.

[0049]

Regarding the polymerization reaction for the manufacturing of the used according to the present invention polyethylene type resin C, that is conducted by using a metallocene type catalyst, because the reaction active points are homogeneous, a resin material is obtained that has the same molecular weight level, and the same degree of branching. Then, it is also a resin material that has no variation in its crystallinity properties. Then, by this reaction, long branched part is synthesized at an equivalent amount. And consequently, the resin material C also, the same way as the resin material B is considered to be a material that has A random branched molecular structure.

[0050]

If the a resin, like the above described polyolefin type resin A according to the present invention, that has a is homogeneous and very finely dispersed state of the amorphous part and a materials such as the polyethylene type resin C, are mixed, the long branched part of the resin C is phase dissolved in the amorphous part of the resin A, that is in a finely dispersed state at a molecular level, and because of that a homogeneous entanglement of the molecular chains occurs without changing the extremely finely dispersed state, and the flexibility properties are maintained. And also, it is anticipated that the stress relaxation properties are increased.

[0051]

Consequently, regarding the film that is obtained from the polyolefin type resin composition material A/B and A/C, and together with that the above described resin composition material, it is a film material that has excellent tensile strength properties, deformation recovery properties, and stress relaxation properties, and together with that it is also equipped with excellent flexibility properties, elongation properties and thermal resistance properties.

[0052]

[Practical Example]

Here below, the present invention will be described in more details by using practical implementation examples. However, the present invention is by no means limited to these practical examples. The evaluation of the parameters according to the practical examples, is conducted according to the described here below.

[0053]

#### (1) Cross separation method

By using a cross separation crossed graph equipment (CFC-150A model: manufactured by Mitsubishi Petrol Company), that is provided with a TREF device and a high temperature GPC equipment, the polyolefin type resin material is measured. The above described TREF method, first, the polyethylene type resin is dissolved in o-dichlorobenzene at a temperature of 140°C or until the complete dissolution of the resin material. And after that, this solution is cooled to a constant temperature, and on the surface of a prepared in advance inert supporting material, a thin polymer layer is formed. After that, the temperature is increased continually or stepwise, and at the desired temperature range, the concentration of the sequentially melted and exiting component, is measured. By the measurement of the component concentration of the above described pre-determined temperature range, it is possible to measure the differences in the molecular crystallinity properties. Namely, at low temperatures, the component that is melting and eluting has low crystallinity properties, and the component that is melting and eluting at high temperatures, has high crystallinity properties.

[0054]

#### (2) Polypropylene structure by an Infra-Red Analysis (FT-IR)

The component that has melted and eluted at a temperature of 90°C or higher according to the above described (1) cross separation method, was separated. This component was contained in a large amount in the polypropylene. By using the Infra-red absorption spectrophotometer (System 200 FT-IR; manufactured by Perkins Elmer Company), the infra-red absorption spectrum of this separated experimental material, was measured. And peaks in the range from the vicinity of 720  $\text{cm}^{-1}$  to the vicinity of 730  $\text{cm}^{-1}$ , were measured, and the structure of the polypropylene that is present as a component of the resin material A, was obtained.

[0055]

((3) is missing from the original - Translator's note.)

#### (4) Extension experiments

By using an extension testing equipment (Tensiron UST -500; manufactured by Orientek Company), the initial length of the experimental sheet sample with a width of 3 mm, (the gap of the clamps) was set at 10 mm, and at the time when this was extended at an extension rate of 200 mm/minute, the stress at break, was measured.

[0056]

(5) Stress relaxation test

By using an extension testing equipment (Autograph AG-500 B: manufactured by Shimazu Company), the initial length of the experimental sheet sample with a width of 3 mm, (the gap of the clamps) was set at 10 mm, and at the time when this was extended at an extension rate of 500 mm/minute, and at the predetermined degree of elongation (25 %), it was maintained in this state for 5 minutes. At the time of this maintaining, the change with the time of the stress limit, was measured, and the residual stress coefficient, was measured according to the described here below formula.

[0057]

Residual stress coefficient  $X = (\text{the stress limit after 5 minutes} / \text{initial stress limit}) \times 100 (\%)$

(6) Measurement of the gel fraction

In approximately 50 ml of xylene, 1 gram of the tested material is immersed, and at a temperature of 120°C, it is dissolved for 24 hours. The undissolved part is filtered by using a 200 mesh metal sieve, and the dried amount of the obtained undissolved fraction is measured. The gel fraction is measured according to the following here below formula.

[0058]

Gel fraction =  $(\text{undissolved weight amount} / \text{initial sheet weight amount}) \times 100 (\%)$

The properties of the polyolefin type resins A and B, that have been used according to the described here below Practical Example 1 ~ 6 and Reference Example 1 ~ 5, are shown in Table 1 and Table 2. In Table 1, the structure of the polypropylene that is contained in the polyolefin type resin A, according to the above described cross separation method and the above described FT-IR method, is presented. In Table 2, the melt extension properties and the gel fraction of the polyolefin type resin material B, are presented.

[0059]

[Table 1]

(S)

1 樹脂 A	2 グレード	3 メーカー名	4 クロス分別法 90℃以上の溶 出成分 (wt%)	5 90℃以上の溶出成分の FT-IRによる ポリプロピレンの構造	6
PO-1	R110E	徳山曹達	10	ランダムポリプロピレン	8
PO-2	T310E	徳山曹達	20	ランダムポリプロピレン	8
PO-3	KS-025	ハイモント	35	ホモポリプロピレン	9

Headings in the table:

1. resin A, 2. grade, 3. name of the maker, 4. melted eluting component (wt %) at a temperature of 90°C and higher, according to the cross separation method, 5. structure of the polypropylene according to the FT-IR of the melted and eluted at a temperature of 90°C or above, component, 6. Tokuyama Company, 7. Himont, 8. random polypropylene, 9. homopolypropylene.

[0060]

[Table 2]

[0060]

\* \* 【表2】

樹脂 B	特徴	メーカー名	a	b	$\eta_a$	$\eta_b$	b/a	$\eta_b/\eta_a$	成分率 (%)
HMS-1	5	ハイモント	0.4	4	$3 \times 10^5$	$1.8 \times 10^5$	10	6	0
HMS-2	7	ハイモント	0.4	4	$1.9 \times 10^5$	$9.0 \times 10^5$	10	4.7	0

Headings in the table:

1. Resin B, 2. properties, 3. name of the maker, 4. gel fraction coefficient (%), 5. homopolypropylene, 6. Himont, 7. random polypropylene.

[0061]

(Practical Example 1)

Relative to the resin material A, the resin material B is mixed at the predetermined amounts as shown according to Table 3, and by using a Brabender Plastograph, this material was melted and mixed at a temperature of 170°C, and by that the composition material was obtained. The units for the mixing ratio presented according to Table 3, are weight %. This resin

composition material is press formed as a 0.4 mm thick sheet at a temperature of 170°C. from this sheet 3 mm wide test sample was prepared, and the above described extension tests and the above described stress relaxation tests, were conducted.

[0062]

The results from the above described tests relative to a resin composition material obtained as 70 weight % of the resin A (PO-2), and 30 weight % of the resin B (HMS-2) were mixed, are presented in Table 3. The results from the described here below Practical Examples 2 ~ 6 and the Reference Examples 1 ~ 5, are also presented in the same Table 3.

[0063]

[Table 3]

		1 実施例						2 比較例				
		1	2	3	4	5	6	1	2	3	4	5
ポリオレフィン 系樹脂 A	PO-1	—	—	—	—	70	—	100	—	—	97	—
	PO-1	70	80	90	80	—	—	—	100	—	—	—
	PO-3	—	—	—	—	—	60	—	—	100	—	40
ポリオレフィン 系樹脂 B (HMS)	HMS-1	—	—	—	20	—	—	—	—	—	—	—
	HMS-2	30	20	10	—	30	40	—	—	—	8	60
物	破断応力 (kgf/cm <sup>2</sup> )	300	280	260	300	220	230	40	180	90	70	280
性	応力残存率 (%)	48	45	45	45	40	40	23	40	20	23	23

(HMS: polyolefin type resin possessing random branched molecular structure)

Headings in the table:

1. Practical Examples, 2. Reference Examples, 3. polyolefin type resin A, 4. polyolefin type resin B (HMS), 5. properties, 6. stress at break (kgf/cm<sup>2</sup>), 7. residual stress coefficient (%).

[0064]

(Practical Examples 2 ~ 6)

The type of the resin A and the resin B and their mixing ratios were changed as shown according to Table 3, and everything else was conducted exactly the same way as described in the technological procedures of the Practical Example 1.

[0065]

(Reference Examples 1 ~ 3)

Only the shown in Table 3 resin material A, was used and the forming and the testing was conducted exactly the same way as described in the technological procedures of the Practical Example 1.

[0066]

(Reference Examples 4 ~ 5)

By using the resin A and resin B, shown according to Table 3, the forming and the testing was conducted exactly the same way as described in the technological procedures of the Practical Example 1.

[0067]

The properties of the polyolefin type resin A and the polyethylene type resin C, that are used according to the described here below Practical Examples 7 ~ 12 and Reference Examples 6 ~ 11, are shown in the above described Table 1 and in the shown here below Table 4. In Table 4, the temperature range according to the cross separation method, the molecular weight distribution and the density, are shown.

[0068]

[Table 4]

(9)

樹脂 C	2 グレード	3 メーカー名	4 クロス分別法 10~100wt%溶出す るまでの温度幅	5 分子量 分布 Mw/Mn	6 密度 g/cm <sup>3</sup>
ポリプロピレン-1 7	EXACT 3027	エクソン・ ケミカル社	10 19℃	2.0	0.900
ポリプロピレン-2 8	EXACT 4011	エクソン・ ケミカル社	10 23℃	2.1	0.885
直鎖状低密度 ポリエチレン(LLDPB)	1004D	出光 石油化学社	11 46℃	4.0	0.925

Headings in Table 4:

1. resin C, 2. grade, 3. maker name, 4. range of the temperature where 10 ~ 100 weight % are melted and eluted according to the cross separation method, 5. molecular weight distribution Mw/Mn, density, g/cm<sup>3</sup>, 7. metallocene PE-1, 8. metallocene PE-2, 9. linear chain type low density polyethylene (LLDPE), 10. Exxon Chemical Company, 11. Shutsuko Petro-Chemical Company

[0069]

(Practical Example 7)

Relative to the resin material A, the resin material C is mixed at the predetermined amounts as shown according to Table 5, and by using a Brabender Plastograph, this material was melted and mixed at a temperature of 170°C, and by that the composition material was obtained. The units for the mixing ratio presented according to Table 5, are weight %. This resin composition material is press formed as a 0.4 mm thick sheet at a temperature of 170°C. from this sheet 3 mm wide test sample was prepared, and the above described extension tests and the above described stress relaxation tests, were conducted.

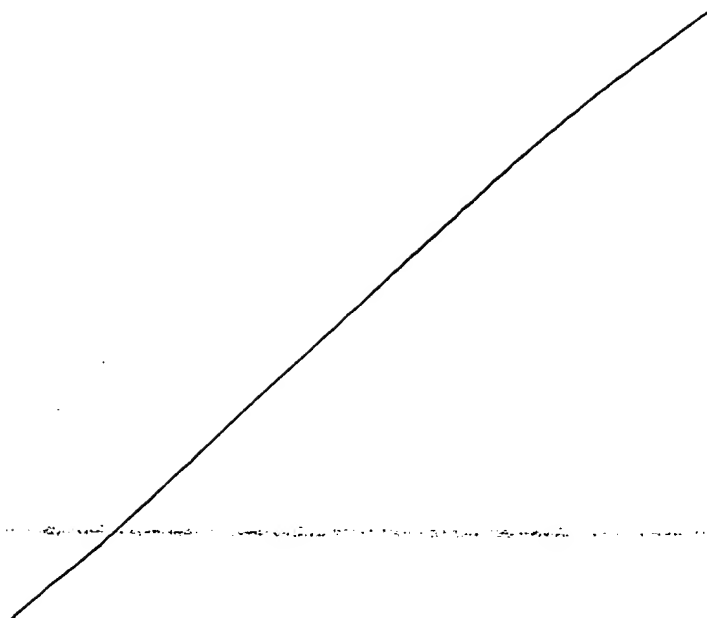
[0070]

The results from the above described tests relative to a resin composition material obtained as 60 weight % of the resin A (PO-2), and 40 weight % of the resin C (Metallocene PE-2) were mixed, are presented in Table 5. The results from the described here below Practical Examples 8 ~ 12 and the Reference Examples 6 ~ 11, are also presented in the same Table 5.

[0071]

[Table 5]

		1 実施例						2 比較例					
		7	8	9	10	11	12	6	7	8	9	10	11
3 系樹脂 A	PO-1	—	—	—	—	70	—	100	—	—	97	—	90
	PO-1	60	80	90	80	—	—	—	100	—	—	—	—
	PO-3	—	—	—	—	—	55	—	—	100	—	40	—
4 系樹脂 C : 系樹脂 PE	系樹脂 PE-1 5	—	—	—	20	—	—	—	—	—	—	—	—
	系樹脂 PE-2 6	40	20	10	—	30	45	—	—	—	3	60	—
7 低密度系樹脂		—	—	—	—	—	—	—	—	—	—	—	10
8 物性	破断応力 (kgf/cm <sup>2</sup> ) 9	190	190	200	200	185	180	80	180	90	70	90	60
	応力残存率 (%) 10	55	59	48	55	45	48	23	40	20	23	25	25



(\* metallocene PE: PE polymerized by using a metallocene catalyst)

(\* low density polyethylene: 1044 D: manufactured by Shutsuko Petro-Chemical Company)

Headings in the table:

1. Practical Example, 2. Reference Example, 3. polyolefin type resin A, 4. polyethylene type resin C: metallocene PE, 5. metallocene PE-1, 6. metallocene PE-2, 7. low density polyethylene, 8. properties, 9. stress at break (kgf/cm<sup>2</sup>), 10. residual stress coefficient (%).

[0072]

(Practical Examples 8 ~ 10)

The type of the resin A and the resin C and their mixing ratios were changed as shown according to Table 3, and everything else was conducted exactly the same way as described in the technological procedures of the Practical Example 7.

[0073]

(Reference Examples 6 ~ 8)

Only the shown in Table 5 resin material A, was used and the forming and the testing was conducted exactly the same way as described in the technological procedures of the Practical Example 7.

[0074]

(Reference Examples 9 ~ 10)

By using the resin A and the resin B, according to Table 5, the forming and the testing was conducted exactly the same way as described in the technological procedures of the Practical Example 7.

[0075]

(Reference Examples 11)

By using the resin A according to Table 5 and a usual low density polyethylene, the forming and the testing was conducted exactly the same way as described in the technological procedures of the Practical Example 7.

[0076]

By this, it was understood that from the above described Practical Example 1, a film was obtained that has especially, improved stress at break and stress relaxation residual coefficient properties. According to the present invention, a film material is obtained that has excellent tensile strength properties, deformation recovery properties, and stress relaxation properties, and it has excellent flexibility properties, elongation properties, and thermal resistance properties.

[0077]

#### **[Results from the present invention]**

According to the present invention, by this, a polyolefin type resin composition material is obtained from which a film material is obtained that has excellent tensile strength properties, deformation recovery properties, and stress relaxation properties, and it has excellent flexibility properties, elongation properties, and thermal resistance properties. The obtained film material can be used as film used for stretch packaging, as a surface protective film, as a stretch film used in grass, as a stretch film used in agriculture, heat shrink films, as adhesive plaster films, as shrink films, etc., and this film can be used widely as a substitute film for the plasticised PVC film.

**Patent Assignee: Sekisui Chemical Industries Company**